

Occurrence of PPCP Contaminants and Screening of Treatment Alternatives for Southeastern Louisiana

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Acknowledgements

Sponsors

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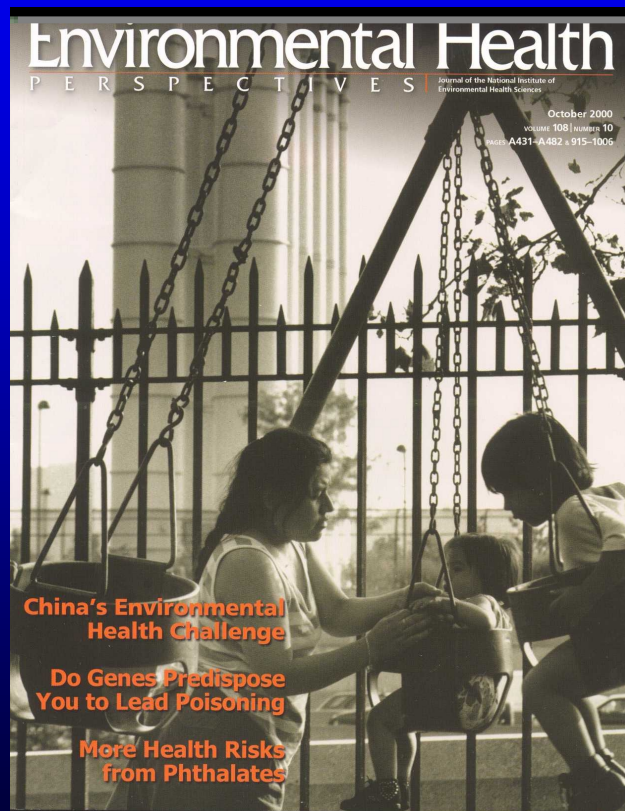
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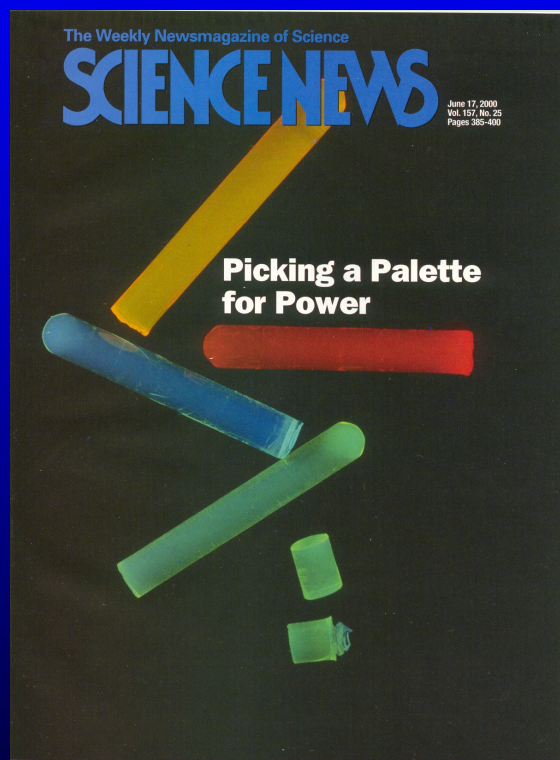


***EXTRA! EXTRA!
Read All About It!***



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EXTRA! EXTRA! Read All About It!



SCIENCE NEWS of the week Excreted Drugs: Something Looks Fishy

Doctors recommend drinking plenty of water to replenish lost fluids and wash away wastes. Just where do the excreted wastes go? At least a few, including hormones and heart drugs, end up in streams—and eventually someone's drinking water, a new study finds.

Though the amounts detected in water from a Louisiana tap were small—just a few parts per trillion (ppt)—they can be biologically active, another study finds.

At these concentrations, one of the hormones measured and another found in birth control pills alter the apparent gender of fish and, possibly, their fertility.

In a suite of yet more studies, collaborating state, federal, and university scientists report finding male carp and walleyes in Minnesota that were producing "sky-high" quantities of vitellogenin, an egg-yolk protein normally made only by females. Such feminization might explain the suspected inability of some adult male fish to make sperm. The researchers had caught the walleyes in the effluent of a sewage-treatment plant—a type of facility that others have shown can release estrogenic pollutants (SN: 3/21/98, p. 187).

Researchers reported all these findings last week in Minneapolis at a meeting sponsored by the National Ground Water Association.

Glen R. Boyd, a civil engineer at Tulane University in New Orleans, described a preliminary survey this spring of the anticholesterol drug clofibrate, the pain reliever naproxen, and the hormone estrone in local waters. His team's sampling turned up the drugs at three sites along the Mississippi River, at four sites around Lake Pontchartrain, and in Tulane's tap water.

Though the drugs weren't always detectable, assays revealed a minimum of 10 ppt of each at least once at every site. Estrone in tap water, for instance, averaged 35 ppt, with a high of 80 ppt.

Environment Canada detected similar pollutants in its 1998 nationwide survey of sewage-treatment effluent. At some sites, estrone reached 400 ppt and the hormone ethinylestradiol from birth control pills reached 14 ppt, notes Chris D. Metcalfe of Trent University in Peterborough, Ontario. He's now exposed eggs of a laboratory fish, the Japanese medaka (*Oryzias latipes*), for 100 days to concentrations typical of the survey.

At exposures of 0.1 ppt ethinylestradiol or 10 ppt estrone, some males became intersex, exhibiting both male and female reproductive tissues. Exposures to 1,000 ppt of either of these estrogens transformed all males into females. The findings are slated to appear in *ENVIRONMENTAL TOXICOLOGY AND CHEMISTRY*.

Though not a North American fish, the medaka models the reproductive responses of native fish well, Metcalfe says. In fact, his findings around the Great Lakes has uncovered signs of intersex white perch. That's worrisome, he observes, since intersex fish "usually aren't interested in sex—in spawning."

Moreover, in early March, his Adelman of the University of Minnesota in St. Paul caught male walleyes in local waters. He was able to extract sperm from all of them except those swimming in a channel that received effluent from a sewage-treatment plant.

The channel's unusual warmth may have triggered these males to release their sperm early, he said. However, he noted, it's also possible that those estrogenic pollutants that fostered males to produce egg-yolk protein also "arrested" the fish in an early state of sexual development." His team is now looking for testicular abnormalities in the fish.

Local carp, which normally spawn later, made sperm. But Adelman reported preliminary data indicating that sperm from males in the sewage-treatment-plant channel show somewhat slowed motility.

None of the new data are strong enough to indict pharmaceutical pollution for harming wildlife, much less people, notes Larry C. Folmar of the Environmental Protection Agency in Gulf Breeze, Fla. However, he adds, the studies by Metcalfe and Adelman hint that estrogens in water may be capable of inducing "functional sterility" in exposed fish.

Christian G. Daughton of the EPA's National Exposure Research Laboratory in Las Vegas says that Boyd's tap water data will be "disturbing" if they're confirmed. "If [drugs] are in drinking water now," he warns, "you can be guaranteed they've been there as long as the drugs have been in use."

—J. Rafiel

Satellite links may don quantum cloaks

Today's most powerful methods for protecting secret communications may not remain secure tomorrow. That's because they rely on the difficulty of making calculations that may someday succumb to faster computers, scientists say. However, secrecy based on the immutable laws of nature—such protection, proven technically feasible—will keep secrets completely in the dark.

Researchers now present the first experimental evidence that laws of quantum mechanics could shield signals all the way from the ground to satellites in low orbit. This potential, claimed for totally secure communications may appeal to military and government agencies, banks, and other security-conscious organizations, says William T. Ruitner of Los Alamos (N.M.) National Laboratory.

In the June 12 *Physical Review Letters*, he and his colleagues describe their recent implementation of quantum key distribution, a step in the transmission of secure communications.

"This is a convincing demonstration," comments William P. Risk of the IBM Almaden Research Center in San Jose, Calif. The Los Alamos researchers "understand the difficult technical challenges associated with [Earth-to-satellite] quantum key distribution and have devised practical ways of overcoming them."

On a New Mexico mesa in daylight, the scientists tested whether they could transmit a code-cloaked in quantum cloaks. They sent it from a twilight laser to a telescope 1.5 kilometers away.

To take advantage of quantum properties, they directed their laser pulses to less than one photon on average—so that many pulses are blanks—and polarized the pulses to represent binary 1s or 0s. Because photons are indivisible, an on-and-off-pulse signaling data would cause a noticeable intensity drop at the receiver. Other aspects of quantum mechanics prevent spies from surreptitiously measuring polarizations or copying them onto other photons (SN: 2/18/98, p. 30).

In normal transmissions of beams, atmospheric turbulence typically causes trouble by scattering and distorting the light. The pulses in the Los Alamos experiment passed through even more turbulence from laser to telescope than they would between a laser on a mountaintop and a satellite, Ruitner says. That's because small eddies, common near the ground but not higher up, disrupt laser beams most strongly.

Despite all that air, the telescope successfully received a randomly generated string of bits, called a key, that serves as a starting code for encoding and decoding messages. Although the key arrived more slowly than data on a cheap fiber-optic phone line connection, even this rate is useful. What makes it so is the security of the link, says coauthor Richard J. Hughes of Los Alamos.

—P. Hase

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SUNDAY Advocate

BATON ROUGE, LA.

JULY 9, 2000

\$1.25

Pharmaceutical pollution: Traces of medicines found in N.O.-area water

Even tiny amounts may affect fish and other aquatic life, researchers say.

By MIKE DUNNE
Advocate staff writer

NEW ORLEANS — Tulane University professor Glen Boyd watches as students Victoria Nwosu and Deante Preston dip a bottle into Lake Pontchartrain and measure a liter of water.

Boyd is searching for pollutants rarely looked for — pharmaceutical drugs.

He has found traces in Lake Pontchartrain, in streams that flow into it, in the Mississippi River and even in tap water in his campus building.

All the pharmaceutical contaminants found were in tiny concentrations of parts per trillion.

While no one knows if such low levels harm human health, some researchers are finding that even such tiny concentrations affect

Tests found more than 50 different pharmaceutical drugs or metabolites — which are forms of the drug after it has been absorbed and expelled — in sewage effluents and surface water. ... 'The question is: What is the toxicological effect of this?' said Christopher Daughton of the Environmental Protection Agency.

fish and other aquatic life.

Traces of antibiotics also may help create resistant bacteria, other researchers say.

Boyd looked only for three common drugs and did not analyze

for traces of antibiotic medications. He found clofibric acid, a cholesterol reducer; naproxen, an anti-inflammatory; and estrone, a form of the female hormone estrogen.

In tests of Mississippi River water taken at three locations in New Orleans, including one spot upstream of the Carrollton Water Works, Boyd and his students found an average of 10 parts per trillion of clofibric acid, an average of 25 parts per trillion of naproxen, and an average of 19 parts per trillion of estrone. One sample on the Mississippi showed 150 parts per trillion of estrone.

In Lake Pontchartrain and streams flowing into it, they found an average of 6 parts per trillion of clofibric acid, an average 10 parts per trillion of naproxen and an average of 19 parts per trillion of estrone. One sample contained up to 190 parts per trillion of estrone.

□ See PHARMACEUTICALS, Page 11A

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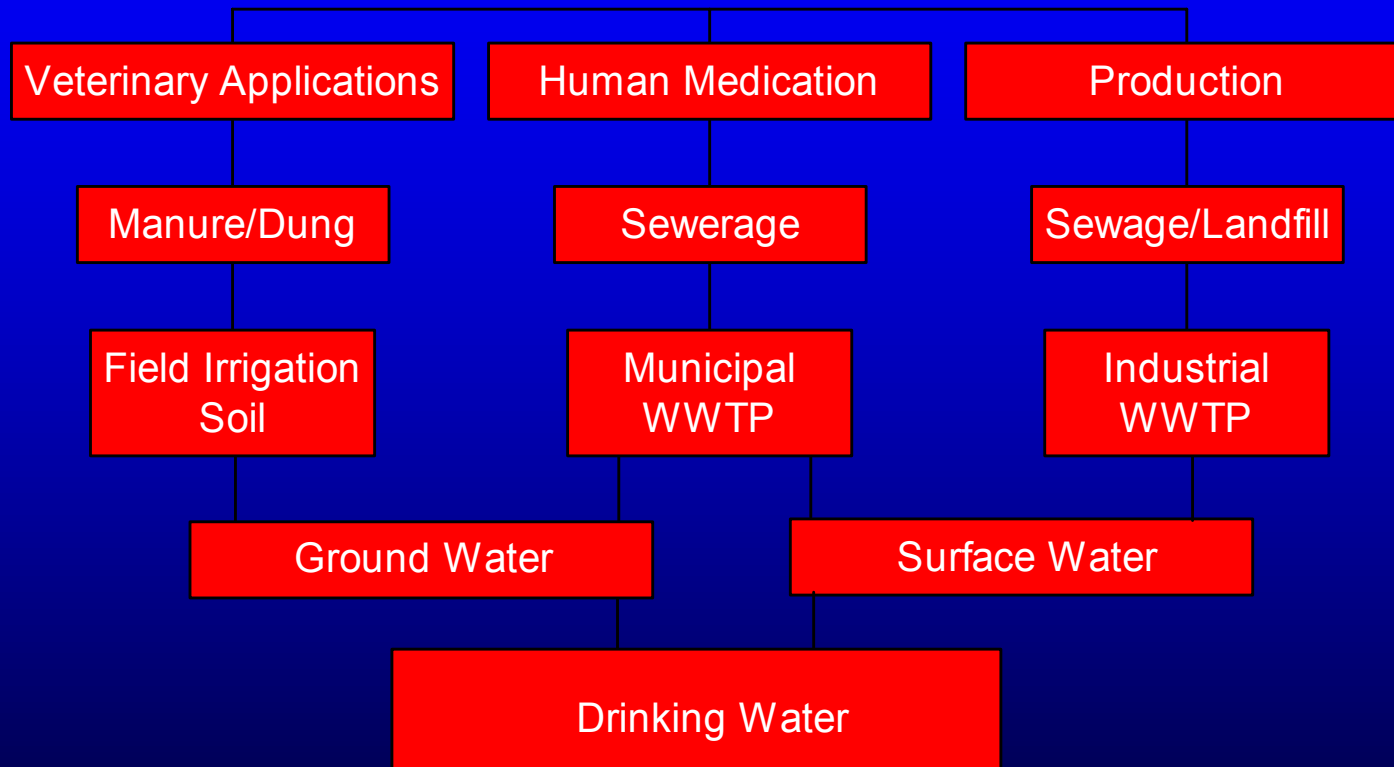


Overview

- **Background**
- **Preliminary Studies**
 - **Methods**
 - **Findings**
- **Current Research**
- **Next Steps**

Background - Sources

Figure 1. Possible PPCP Sources and Pathways



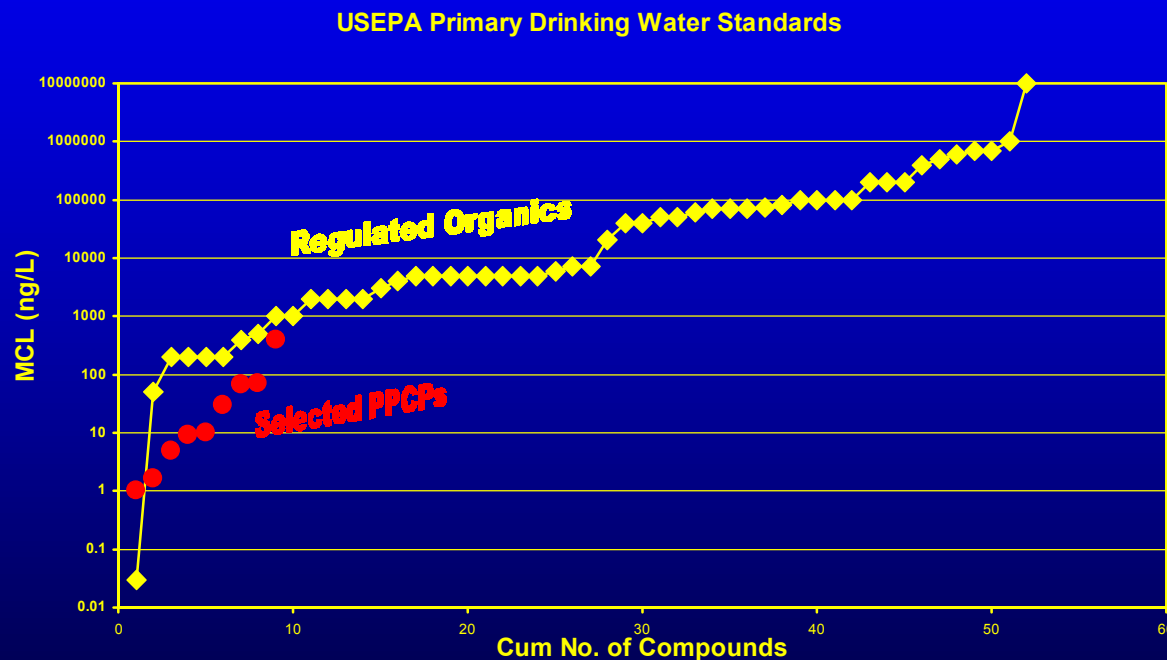
Background – International Perspective

Investigation	Clofibric Acid (µg/L)	Naproxen (µg/L)	Estrone (µg/L)
Germany rivers & streams (Ternes, 1998)	0.066 to 0.070	-	<0.0005 to 0.0016
Brazil surface waters (Stumpf et al., 1999)	<0.01 to 0.03	<0.01 to 0.39	-
Swiss lakes & North Sea (Buser et al., 1998)	0.001 to 0.009	-	-

Other investigations conducted in Denmark, Israel, Canada and USA.

Background – Current DW Regulations

Existing regulations generally are 10 to 1000 times greater than detectable PPCPs in the aquatic environment.



AWWA. 1999. *Water Quality & Treatment*, McGraw-Hill, NY.

Current DW Regulations

SDWA Amendments of 1996

Food Quality Protection Act of 1996

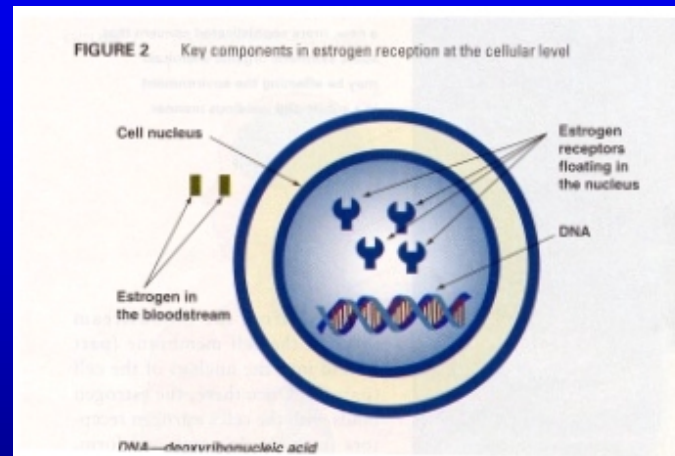
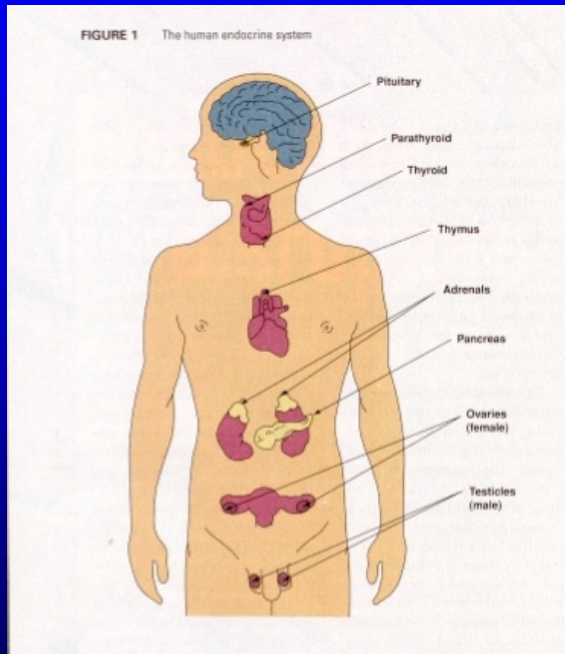
USEPA (1996) – Endocrine Disruptor Screening and Testing Advisory Committee

Report (1998)

- **62,000 possible EDCs**

Ref: www.awwa.org/endocrine/

Endocrine System & Disrupting Chemicals



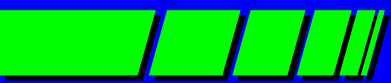
EDCs interfere with the normal function of the endocrine system

Trussell, R.R. 2001. Endocrine disruptors and the water industry, *JAWWA*, 93(2):58-65

Current DW Regulations

- **SDWA currently regulates suspected EDCs:**
 - **Pesticides (8 MCLs)**
 - **Nonpesticides organics (4 MCLs)**
 - **Inorganic chemicals (Cd,Pb,Hg MCLs)**
- **MCLs defined by toxic/cancer effects**
- **If adverse effects to endocrine system is determined to be lower, then MCL can be changed**

Ref: www.awwa.org/endocrine/



EDCs & PPCPs – Drinking Water Concern?

- Pharmaceuticals and personal care products (PPCPs) - typically included in EDC discussion
- Occurrence of EDCs and PPCPs - widely unknown
- Lack of monitoring - especially in the USA

Ref: www.awwa.org/endocrine/

Background – USA Emerging Env Issue

Gov. Agencies

- U.S. EPA
- U.S. Geo Survey

Prof. Organizations

- AWWA
- WEF
- NGWA

Research

- Tulane Univ.
- Michigan State U. & Lk. Mead, Nevada
- UC Berkeley
- Colorado State Univ.
- Georgia Tech
- Others



PPCPs – Local Environmental Concern?

- **Occurrence of PPCPs in Water Resources?**
 - **Mississippi River**
 - **Lake Pontchartrain**
- **More Research is Needed**



PPCPs – Health & Environmental Concern?

- **Low-level PPCP concentration (ng/L)**
 - **Chronic exposure (?)**
 - **Human health (?)**
 - **Ecological health (?)**
- **More Research is Needed**



PPCPs – Is Treatment Needed?

➤ Existing technologies

- Activated carbon
- Enhanced coagulation
- Oxidation (e.g., O_3 , H_2O_2 , UV)
- Membrane filters
- Other

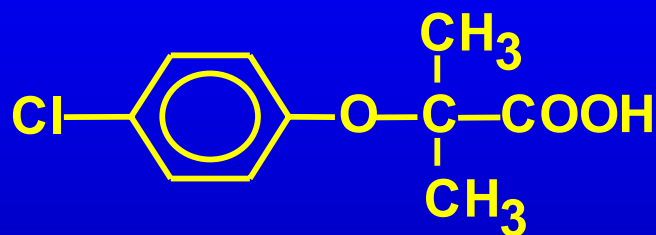
➤ More Research is Needed



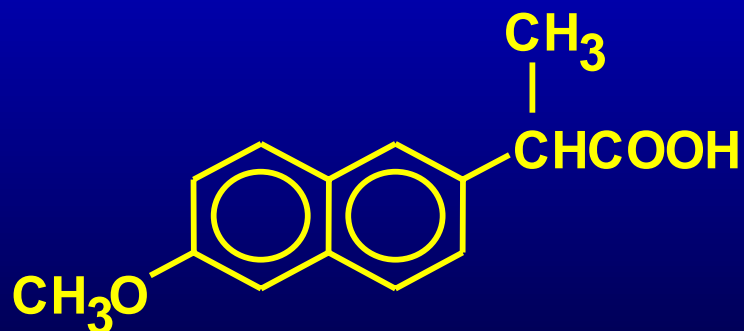
Hypothesis

- Pharmaceutical contaminants persist in the Mississippi River and local aquatic environs.
- Pharmaceutical contaminants potentially can be treated using existing treatment technologies.

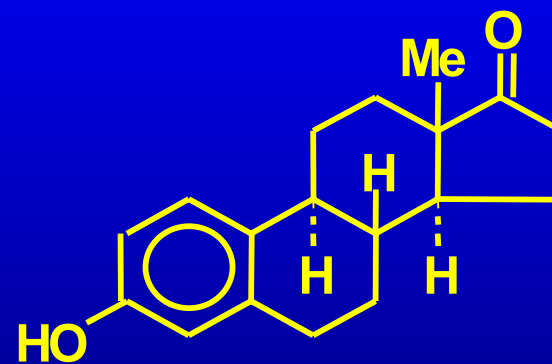
Selected Pharmaceutical Contaminants



Clofibric Acid



Naproxen



Estrone

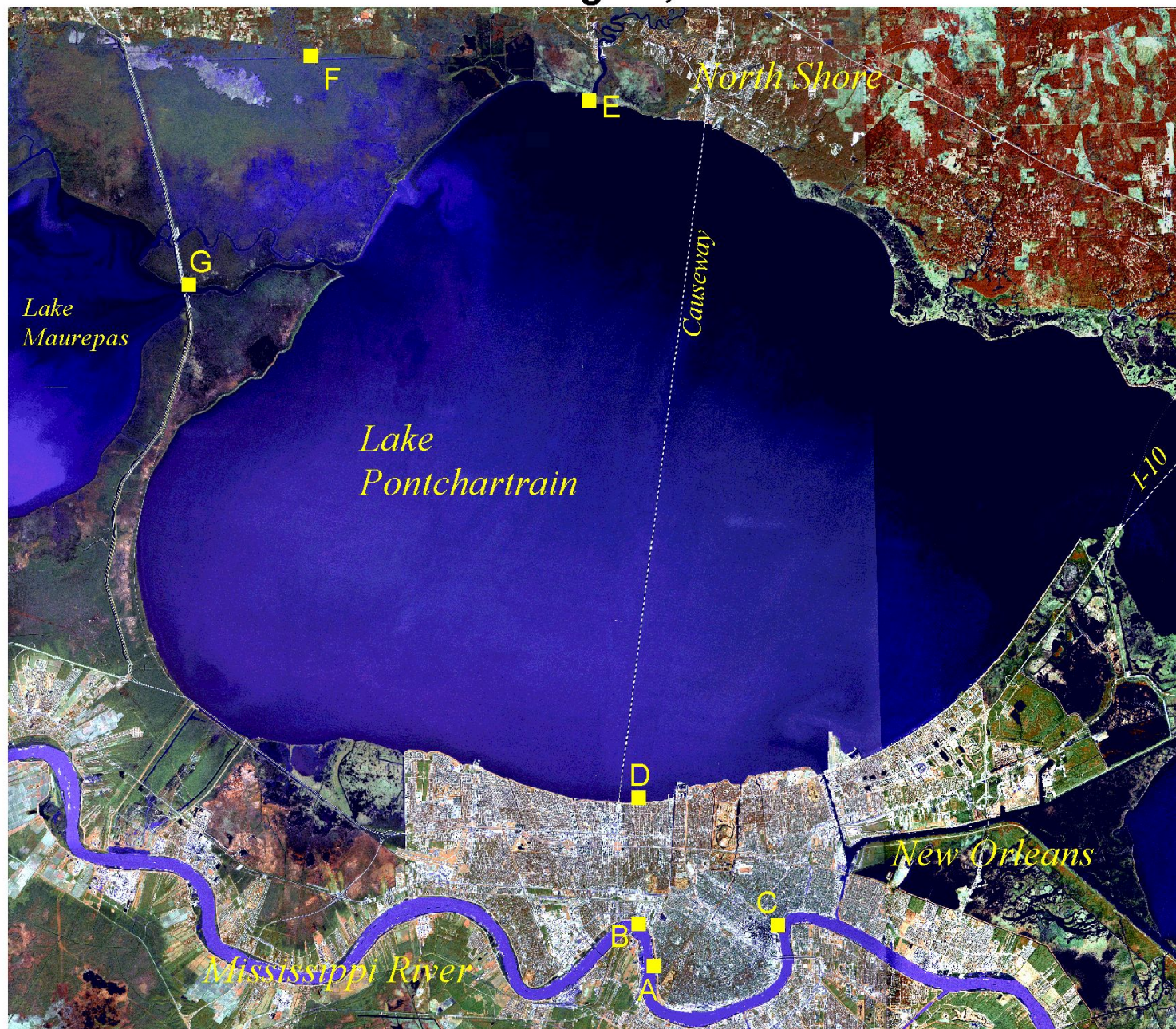


Methods - Field Sampling

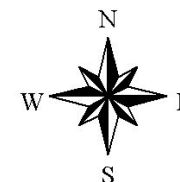
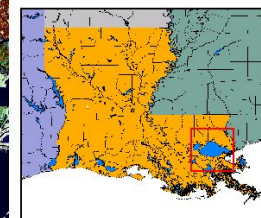
- **Weekly sampling**
 - Mississippi River
 - Lake Pontchartrain
- **Surface grab samples**
- **Water quality parameters**
(pH, temp, alk, TDS)

Pharmaceutical Sampling Sites in the Greater New Orleans Region, Louisiana

5 0 5 10 Miles



Samples collected
February 4 to
March 31, 2000



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Methods - Field Sampling



Methods - Field Sampling





Methods - Treatment Testing

➤ Materials

- Clofibric acid, naproxen & estrone
- Pulverized GAC
- Distilled water

➤ Bench-top shaker

➤ Vacuum filtration

Methods - Treatment Testing



Methods - Lab Analysis

- **Solid phase extraction**
 - Conditioned Biobeads SM-2
 - DCM fraction collected & dried
- **TMS derivatization**
 - 100 μ L sample + 500 μ L of BSTFA (99%) and TMCS
- **GC/MS**
 - +EI with Internal Standard
 - Selected Ion Monitoring (SIM)

Methods - Lab Analysis



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Methods - Lab Analysis



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Mississippi River – Preliminary Findings

Median Concentration*				
Sampling Site		Clofibric Acid (µg/L)	Naproxen (µg/L)	Estrone (µg/L)
A	Barge at USACE	0.01	0.01	<0.01
B	River Rd at Harding Ave	0.005	0.005	0.01
C	Decatur at Toulouse	0.01	0.02	<0.01

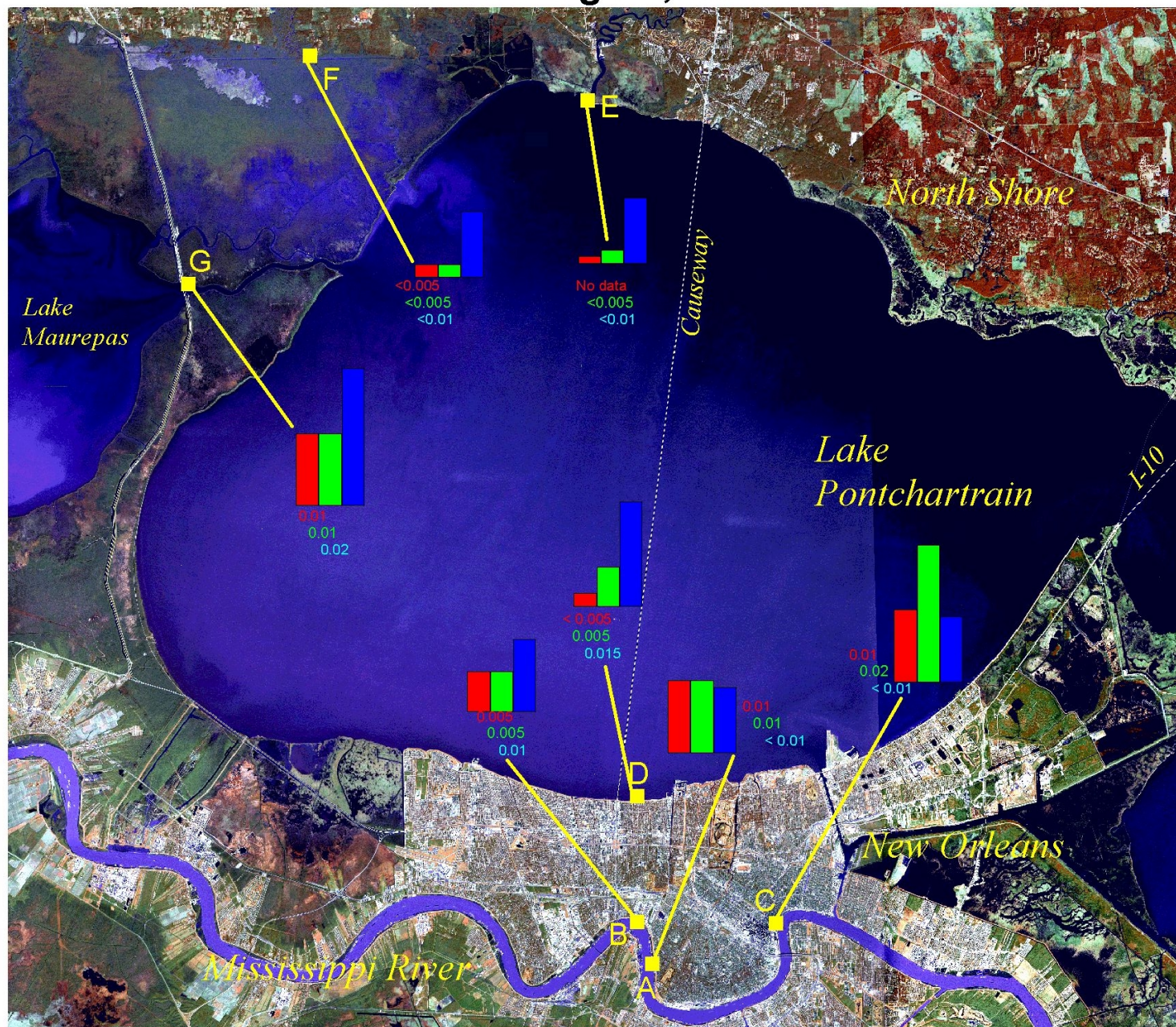
* Based on samples collected from February 4 through March 31, 2000. Method detection limits were 0.005 µg/L for clofibric acid and naproxen and 0.01 µg/L for estrone.

Lake Pontchartrain – Preliminary Findings

Median Concentration*				
Sampling Site		Clofibric Acid (µg/L)	Naproxen (µg/L)	Estrone (µg/L)
D	Bonnabel Marine Sta	<0.005	0.005	0.015
E	Tchefuncta R. at Madisonville	ND	<0.005	<0.01
F	Tangipahoa R. at State Rt 445	<0.005	<0.005	<0.01
G	Pass Manchac at L. Maurepas	0.01	0.01	0.02

* Based on samples collected from February 4 through March 31, 2000. Method detection limits were 0.005 µg/L for clofibric acid and naproxen and 0.01 µg/L for estrone.

Pharmaceutical Sampling Results in the Greater New Orleans Region, Louisiana

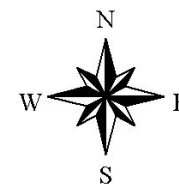
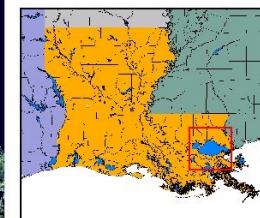


Legend

- B Sample Site
- Clofibric Acid
- Naproxen
- Estrone

Samples collected
February 4 to
March 31, 2000

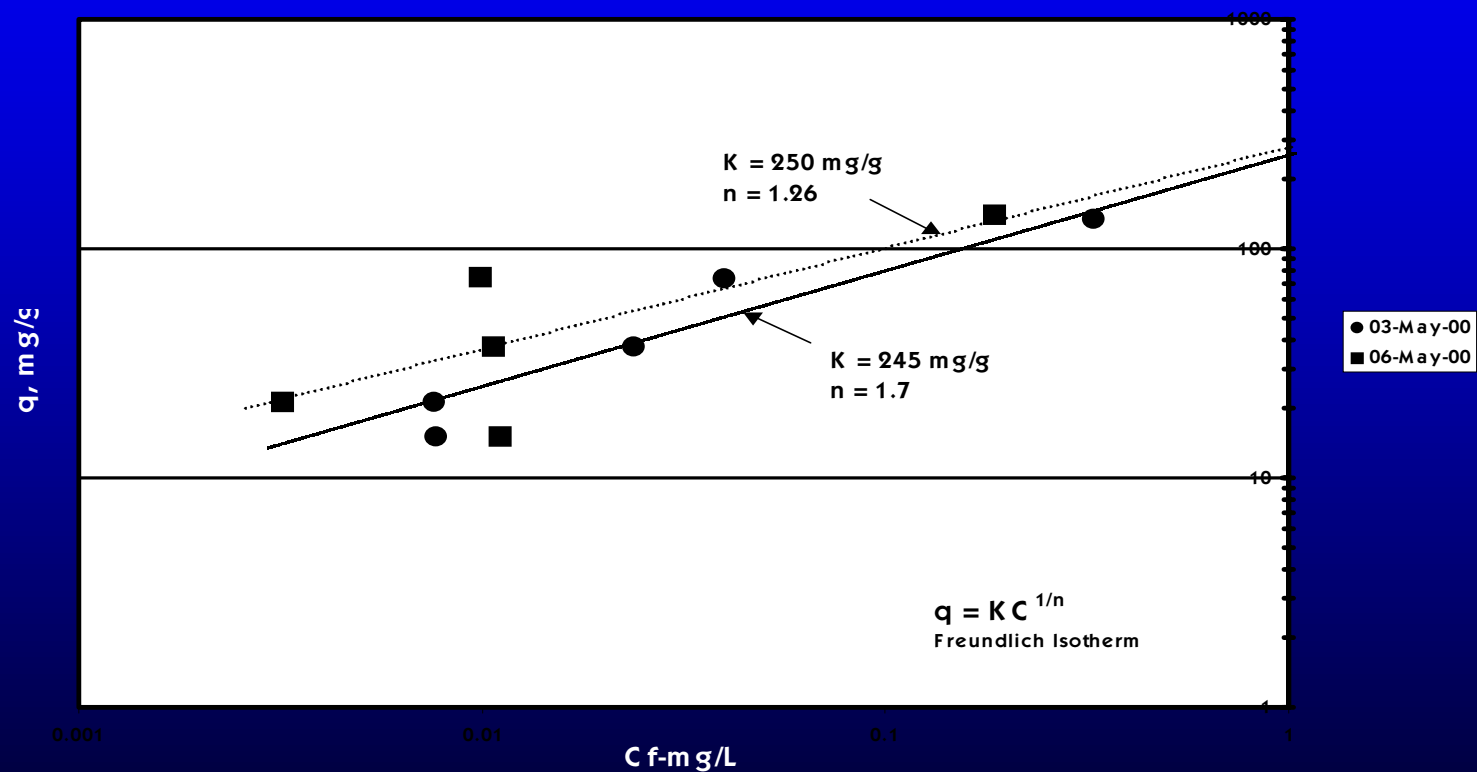
Median occurrences ranged
from < 0.005 to 0.02 uG/L



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GAC Testing - Preliminary Findings





Preliminary Conclusions

- **Pharmaceutical contaminants have been detected at low levels in the Mississippi River and Lake Pontchartrain.**



Preliminary Conclusions (continued)

- **Pharmaceutical contaminants potentially can be removed from water by activated carbon adsorption.**



Discussion

- The health and environmental significance of pharmaceutical contaminants detected in the Mississippi River and Lake Pontchartrain is not known.

Current Research - Objectives

- **Refine analytical techniques**
- **Expand list of target compounds**



Current Research – Analytical Methods

- **Optimize solid phase extraction**
- **Optimize TMS derivatization**



Current Research – Analytical Methods

Target Compound	Type	Estd Method DL (ng/L)*
Clofibric acid	Lipid regulator	3
Estrone	Steroid	3
17 β -Estradiol	Steroid	1
Ibuprofen	Analgesic	13
Naproxen	Analgesic	3
Acetaminophen	Analgesic	45
Bisphenol A	Fungicide & disinfectant	0.6
Chlorophene	Fungicide & disinfectant	0.6
Triclosan	Fungicide & disinfectant	1
Fluoxetine	Antidepressant	178
Caffeine	Human activity marker	24

* Based on IDLs for a 2 μ L injection from a 100 μ L extract of a 1L sample and assuming 100 percent recovery.

Current Research – Treatment

- Test O₃ effectiveness
 - 17β-Estradiol
 - Bisphenol A
 - Naproxyn
- Test carbon adsorption
 - Clofibric acid (Hartwick Coll.)
 - Other (Summer Interns)

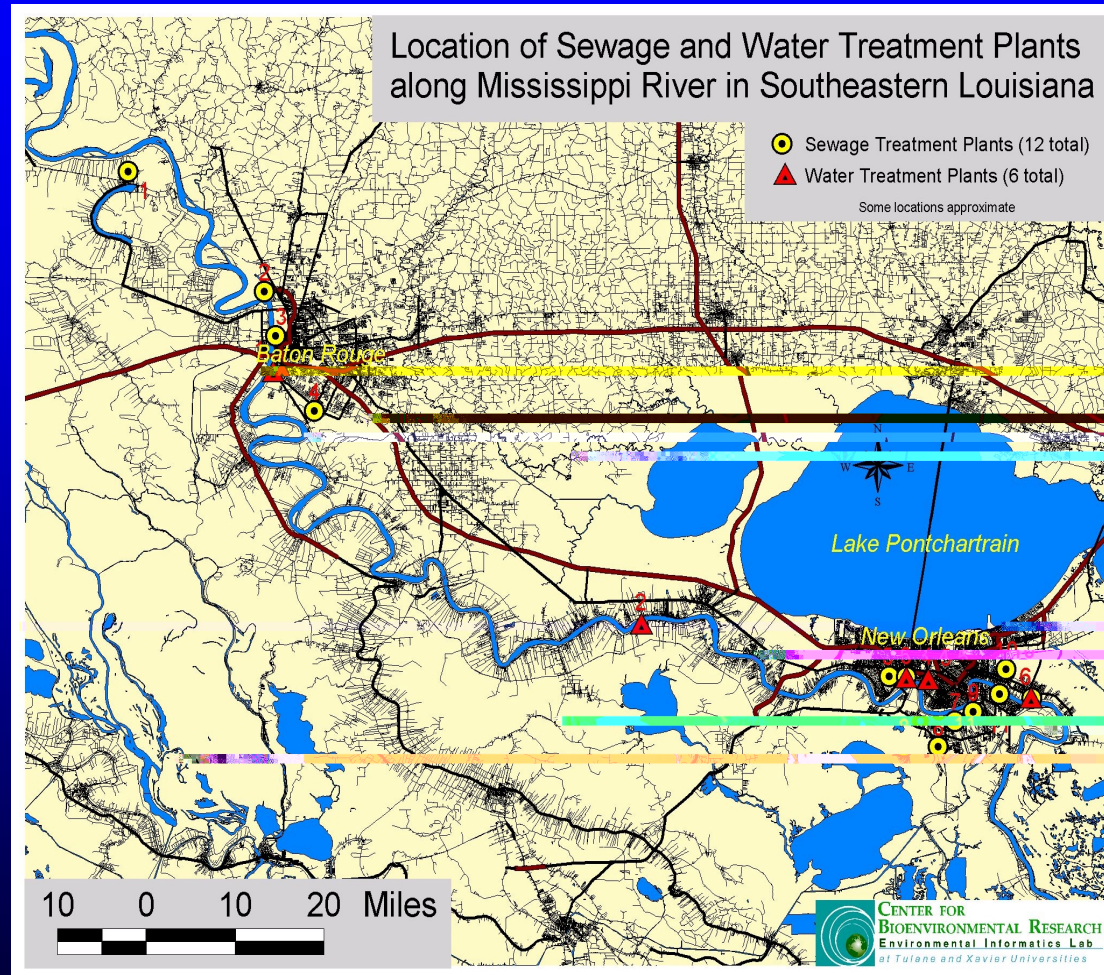




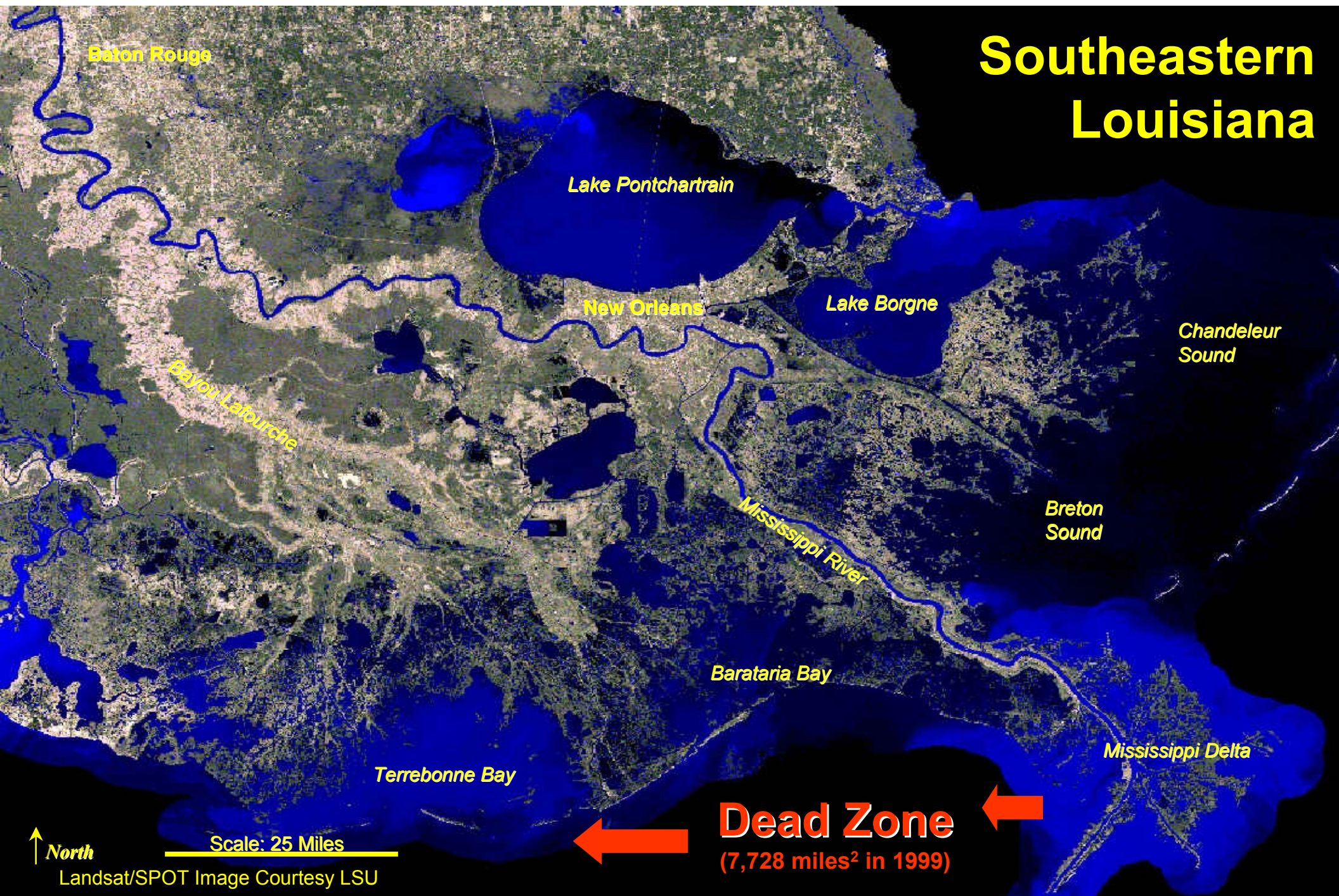
Next Steps

- **Expand further list of target compounds**
- **Develop sediment extraction method**
- **Continue and expand field sampling program**

Next Steps (continued)



Southeastern Louisiana





Next Steps (continued)

- **Evaluate further treatment alternatives**
 - **Conventional treatment**
 - **Activated carbon**
 - **Enhanced coagulation**
 - **Oxidation**
 - **Membranes**

Next Steps (continued)

Develop Collaborations

- **Treatment effectiveness**
(e.g., utilities, universities & consultants)
- **Occurrence and environmental significance**
(e.g., EEB, GIS)
- **Health significance**
(e.g., SPH, EHS)



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